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Thermal and spectroscopic investigation of sol-gel derived aluminosilicate bioglass matrices

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Aluminosilicate samples obtained by sol-gel route, using as SiO_2 source silicic acid or tetraethylorthosilicate (TEOS) are investigated by differential thermal analysis and infrared spectroscopy. Thermal analysis points out that the removal of free water takes place at significant lower temperature for samples prepared with silicic acid. Infrared active functional groups were identified from FT-IR spectra. The shift to lower wavenumbers recorded for IR absorption bands corresponding to Si-O-Si bonds and Al-O vibrations as the samples are prepared with TEOS as SiO_2 source show a stiffer and more disordered network in these samples as compared with that of the samples obtained with silicic acid.

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1. Introduction

Radiotherapeutic glass spheres (glass beads) are used to treat liver cancer, among other medical applications [1]. The glass beads are made from aluminosilicate glass that contains yttrium oxide or oxide of a rare earth element activable by neutron irradiation. Once irradiated, the beads emit beta radiation to malignant cells within the liver. They can also incorporate iron oxide which as a result of a proper heat treatment can crystallise as magnetite in the vitroceramic sample that becomes a potential biomaterial for hyperthermia [2, 3].

Aluminosilicate glass matrices are also largely present in endosseous implant composites [4]. Numerous works deal with the influence of alumina/silica or alumina/silicon solid state reactions on features of electronic devices [5, 6]. Development of aluminosilicate mesoporous materials with microporous properties is of great interest in the field of catalysts and adsorption [7].

Sol-gel method is an easy way to produce high purity glass systems at room temperature and are frequently used for preparing glasses and glassceramic powders [8]. Glass samples obtained by sol-gel route offer the advantage of high chemical homogeneity and lower preparation temperature especially as compared with the glasses of the same composition obtained by melting method. Some of the most interesting applications of the sol–gel method include the synthesis of fine nanoparticles [9].

This study is focused on thermal and IR analyses of Al_2O_3-SiO_2 binary system obtained following the sol-gel route.

2. Experimental procedure

Reagent-grade tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$,) or silicic acid ($SiO_x(OH)_{4-2x}$) and aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ were used as starting materials to prepare by sol-gel process $Al_2O_3 \cdot 2SiO_2$ and $Al_2O_3 \cdot 3SiO_2$ samples. A few drops of concentrated nitric acid and then of concentrated ammonia have been added to the water solutions of the samples prepared with TEOS. The sludges were stirred for about 30 minutes and the precipitates were filtered and washed in decationised water. White solid sample were obtained after drying at 110°C.

White powder samples were haracterized using thermal and infrared spectroscopic analyses. Infrared spectroscopic analysis was carried out also on samples heat treated in air at 950°C, under normal pressure. The X-ray diffraction patterns were obtained by means of standard DRON powder diffractometer.

For thermal investigation the thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves were recorded with a heating rate of 10 °C/min on a MOM type derivatograph.

Fourier Transform Infrared (FTIR) spectroscopic analysis was conducted using Bruker instrument (Equinox 55) with a resolution of 2 cm^{-1}, at room temperature using the KBr disk technique.

3. Results and discussion

The sol gel samples are in vitreous state as indicate X-ray powder diffraction patterns which consist of a single broad peak and do not reveal any crystalline phase in the as prepared samples.

The thermal analysis results show that all the weight loss take place below 300°C, above which no more significant weight loss occurred (Fig. 1).

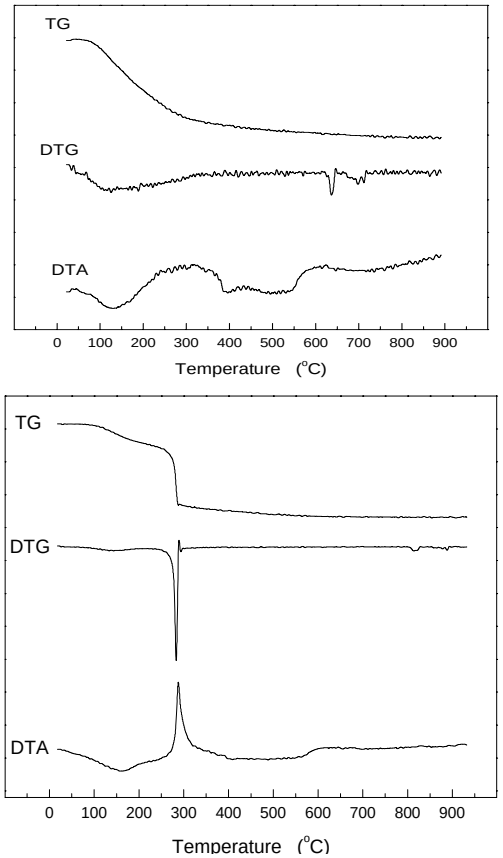

Fig.1. Thermal analysis plots for $Al_2O_3{\cdot}2SiO_2$ prepared with silicic acid (a) and $Al_2O_3{\cdot}3SiO_2$ prepared with TEOS (b).

A broad endothermic peak is observed in DTA curves (Fig. 2) in the temperature range 130-160°C and is attributed to the removal of physically adsorbed water. The mass loss is about 30 % for samples prepared with silicic acid and 50% for those prepared with TEOS.

Thermal analysis points out also that the removal of free water takes place at significant lower temperature for samples prepared with silicic acid (Fig. 2). By further heating a second mass loss is well evidenced in TG and DTG curves but only for samples prepared with TEOS. This mass loss is due to the removal of organic part entering the tetraethylorthosilicate.

In DTA runs of these samples is recorded around 300°C an exothermic event well developed for samples prepared with TEOS and very large for those prepared with silicic acid. This exothermal peak may represent a dehydroxylation reaction [10]. A second exothermic weak peak occurs around 600°C, due to the transformation from gel to glass [11].

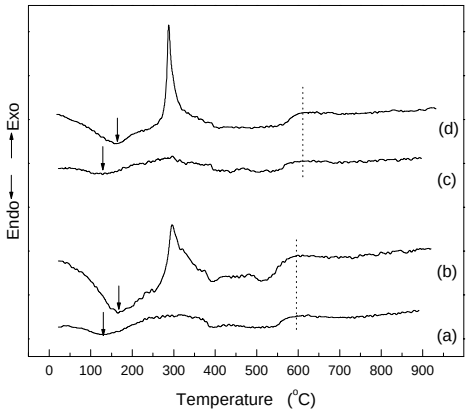

Fig. 2 DTA plots for $Al_2O_3{\cdot}2SiO_2$ and $Al_2O_3{\cdot}3SiO_2$ sol-gel derived sample prepared with silicic acid (a, c) and TEOS (b, d), respectively.

FTIR analysis shows spectroscopic changes both for $Al_2O_3{\cdot}2SiO_2$ (Fig. 3) and $Al_2O_3{\cdot}3SiO_2$ (Fig. 4) when they are prepared with silicic acid or TEOS as silicon sources. The presence of water is indicated by the broad bands at 3400, 3100 and 1640 cm^{-1}. The spectra of the investigated samples contain specific information mainly between 400 cm^{-1} and 2000 cm^{-1}.

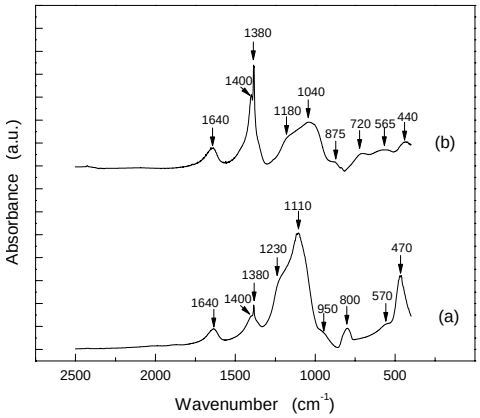

Fig. 3. FTIR spectra recorded from $Al_2O_3{\cdot}2SiO_2$ sol-gel samples prepared with silicic acid (a) and TEOS (b).

The small intensity band at 1640 cm^{-1} is mainly connected with the bending vibrations of the H–OH bond from adsorbed water [12]. The 1380 cm^{-1} band is assigned to N-O stretching vibration [13] and indicates the presence of NO_3^- species resulting from thermal decomposition of aluminum nitrate. Other nitrogen species are also occurring, as reflected by the larger band centered at 1400 cm^{-1} [14]. The intensity of this band is much higher in the case of using TEOS as SiO_2 source, when also ammonia has been added to the starting solution.

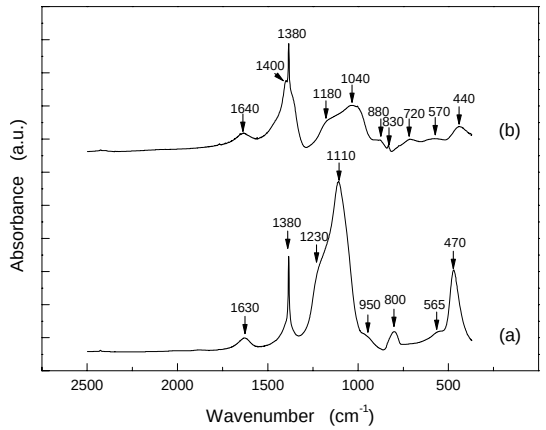

Fig. 4 FTIR spectra recorded from $Al_2O_3 \cdot 3SiO_2$ sol-gel samples prepared with silicic acid (a) and TEOS (b).

The IR bands attributed to vibrations involving SiO_4 units are usualy located in the spectral region under 500 cm^{-1} and between 900 and 1300 cm^{-1} [15, 16]. According to Moreno et al. [17] infrared absorption bands of silica lattice occur at 460, 798, 960, 1084 and 1176 cm^{-1}. Other authors [18] consider that in aluminosilicates obtained by sol-gel method a peak at 1049 cm^{-1} is referring to Si–O–Si, while a peak at 1102 cm^{-1} is corresponding to Al–O–Al bonds.

In our samples the IR bands located at 470 cm^{-1} in the case of samples prepared with silicic acid and at 440 cm^{-1} in the case of samples prepared with TEOS are related to bending vibrations of Si-O-Si bonds. The large bands around 1100 cm^{-1} are assigned to stretching vibration of Si-O-Si bonds and to Al–O–Al bonds.

The correlation between IR absorption bands and different types of aluminate polyhedra is based on IR results obtained for aluminate crystals [12, 19]. The Al-O stretching vibrations of tetrahedral AlO_4 groups are related with the bands in the region 900 – 750 cm^{-1} and the IR absorption bands situated in 650 – 500 cm^{-1} region are associated with stretching modes of AlO_6 octahedra. Between these two relatively large spectral regions some bands could appear for the compounds with pentacoordinated aluminum [20,21].

In the case of our samples, the band at 570 cm^{-1} is assigned to Al-O vibrations in AlO_6 and that from 800 cm^{-1} to AlO_4 units. As can be observed from Figs. 3 and 4, the bands assigned to silicium and aluminum structural units are shifted to lower wavenumbers for the samples prepared with TEOS. This shift and the less resolved bands show a much stiff and disordered network in the samples prepared with TEOS. Beside this shift, one also remarks a new weak absorption band at 830 cm^{-1}, that becomes more evident for the samples with higher Al_2O_3 content (Fig. 3-5).

The spectral feature for $Al_2O_3 \cdot 2SiO_2$ and $Al_2O_3 \cdot 3SiO_2$ samples are very similar if the same SiO_2 source is used (Fig. 5 and 6), showing that the change of aluminum/silicium ratio practically does not affect the structural units that are building the samples network.

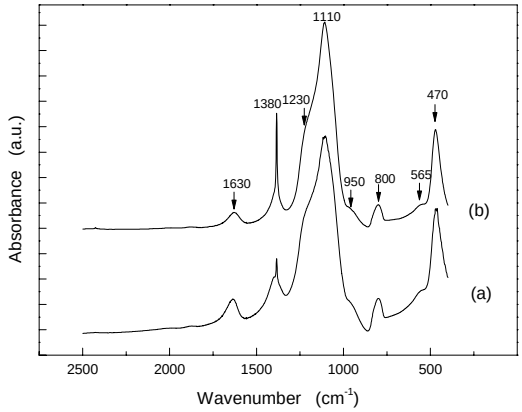

Fig. 5. FTIR spectra recorded from $Al_2O_3 \cdot 2SiO_2$ (a) and $Al_2O_3 \cdot 3SiO_2$ (b) sol-gel samples prepared with silicic acid.

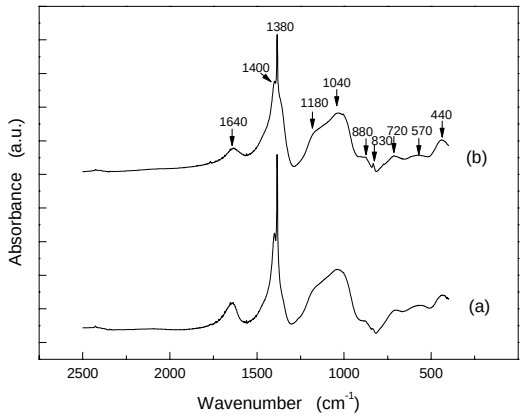

Fig. 6 FTIR spectra recorded from $Al_2O_3 \cdot 2SiO_2$ (a) and $Al_2O_3 \cdot 3SiO_2$ (b) sol-gel samples prepared with TEOS.

In Figs. 7 and 8 are shown the IR spectra of the samples prepared with silicic acid, before and after their thermal treatment at 950°C. Similar results are obtained also for the samples prepared with TEOS.

The applied heat treatment does not lead to sample crystallisation, because neither new absorption bands nor a peak narrowing is occurring. This result is also evident from the differential thermal runs which do not evidence exothermic crystallisation peaks up to 1000°C. The main change is the almost complete disappearance of the band typical to notrogen species around 1400 cm^{-1}. The framework structure of the investigated aluminosilicate samples is realized by joining tetracoordinated SiO_4 structural units with preponderantely tetracoordinated AlO_4 units.

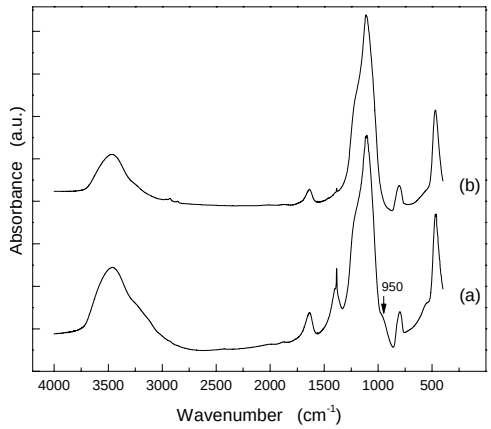

Fig. 7. FTIR spectra of as prepared (a) and heat treated at 950°C (b) $Al_2O_3 \cdot 2SiO_2$ sol-gel samples with silicic acid.

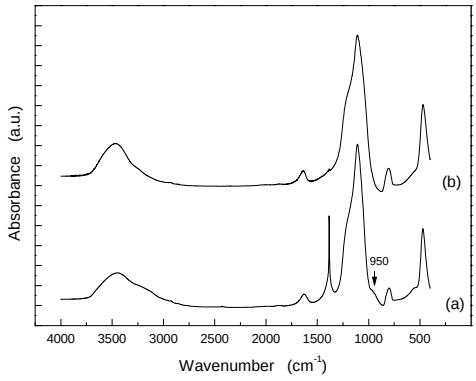

Fig. 8. FTIR spectra of as prepared (a) and heat treated at 950°C (b)$Al_2O_3 \cdot 3SiO_2$ sol-gel samples with silicic acid.

4. Conclusions

Thermal analysis points out that the removal of free water takes place at significant lower temperature for aluminosilicate samples prepared with silicic acid by using the sol-gel route. Infrared active functional groups were identified from FT-IR spectra are SiO_4 and AlO_4 units. The shift to lower wavenumbers recorded for IR absorption bands corresponding to Si-O-Si bonds and Al-O vibrations as the samples are prepared with TEOS as SiO_2 source show a stiffer and more disordered network in these samples as compared with that of the samples obtained with silicic acid as SiO_2 source. The heat treatment applied at 950°C does not lead to development of crystalline phases. The major effect consists in removal of nitrate rests, as indicates the disappearance of 1380 cm^{-1} band typical of N–O stretching vibration.

Acknowledgement

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